

PATENT SPECIFICATION

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(54) TIN ELECTRO-PLATING SOLUTION

(71) We, SUMITOMO ELECTRIC INDUSTRIES, LTD., a Japanese Body Corporate, of, 15, Kitahama 5-chome, Higashi-ku, Osaka, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a novel tin-electroplating solution.

Tin-plating solutions that have previously been used are mostly a sulphuric acid bath or fluoborate bath. However, a sulphuric acid bath has a limitation that about 10 A/dm² is the maximum value of cathode current density for it, while a fluoborate bath has the disadvantage that it is difficult to remove fluorides and borides when disposing of the waste liquid and that the solution is strongly corrosive.

The present invention relates to a tin-plating solution (1) which contains from 30 to 300 g/l of sulphamate ions, 15 to 300 g/l of divalent tin ions, and 5 to 100 g/l of an aromatic sulphononic acid having either an —OH radical or an —OH radical and a —CH₃ radical on the aromatic nucleus, or a salt thereof. A non-ionic or anionic surface active agent may be added to the afore-mentioned plating solution (1). Furthermore, animal glue or gelatin may be added to the plating solution (1).

The source of sulphamate ions may be any compound that produces sulphamate ions in an aqueous solution. For example, sulphamic acid, sodium sulphamate, potassium sulphamate or ammonium sulphamate may be used. The concentration of sulphononic acid ions is from 30 to 300 g/l. If it is less than 30 g/l, the concentration of tin in the plating electrolyte cannot be maintained sufficiently high and the electric conductivity is poor. A concentration in excess of 300 g/l will not have any particular adverse effect, but such a concentration is unnecessary.

The divalent tin may be added in the

form of stannous oxide, stannous sulphate or stannous chloride, and the concentration of divalent tin ions is from 15 to 300 g/l. If the concentration is less than 15 g/l, the electro-deposited tin will not have a sufficiently good smoothness, and the cathode current density cannot be maintained high enough. A concentration in excess of 300 g/l will not have any particular adverse effect, but the loss of tin carried out by the solution is great. Usually, therefore, it is advisable to use a concentration within the afore-mentioned range.

The aromatic sulphononic acid is preferably cresol sulphononic acid, phenolsulphononic acid, naphthol sulphononic acid, or a salt thereof. The concentration is from 5 to 100 g/l. If the concentration is less than 5 g/l, their stabilizing effect will not be sufficiently high. A concentration in excess of 100 g/l will have no particular adverse effect, but such a concentration is unnecessary. The salts of these acids, for example, the sodium salts and potassium salts, are also effective when used in a concentration within the above range.

Furthermore, their ortho-, meta- and para- isomers are also similarly effective. Generally, these products are synthesized as mixtures of such isomers, and it is possible to use them regardless of whether they are in the form of a mixture or whether they are in the form of a single product.

Examples of non-ionic surface active agents are polyethyleneglycol-nonyl phenyl ether, polyethyleneglycolisooctyl ether and polyethyleneglycol-lauryl ether. Particularly preferred are those in which the ethylene oxide addition mol number is 5 or more, since those in which the number is less than 5 have poor solubility in water. Examples of anionic surface active agents are sodium *n*-octyl sulphate and others. If the concentration of the surface active agent, in terms of its pure component, is 1 g/l or more, its smoothening effect is usually remarkable. If the concentration is less than 1 g/l, it still has a smoothening effect,

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but the effect is generally not sufficient. If the concentration is in excess of 30 g/l, it does not present any particular problems with respect to the properties of the electro-deposited layer, but such a concentration enhances the foaming property of the plating solution and is unnecessary.

It is also possible to obtain a smooth electro-deposit by using animal glue or gelatin instead of using a surface active agent. The optimum quantity of glue or gelatin to be added is from 1 to 10 g/l. Its addition in a quantity outside of this range does not present any particular difficulty, but a sufficient smoothening effect can be expected from an addition of a quantity within the above range.

When plating is effected with the tin plating solution of the present invention, preferably a temperature within the range of from 5 to 80°C is used and an electric current density within the range of from 1 A/dm² to 100 A/dm² is employed. Preferably, when the electric current density is not less than 2 A/dm², stirring should be carried out.

The present invention will be described in further detail with reference to the following Examples.

Example 1

Divalent tin (as stannous oxide)	70.2 g/l
Sulphamic acid	210 g/l
Polyethylene glycol nonylphenyl ether (ethylenoxide average addition mol number 14)	20 g/l
Orthocresol sulphonic acid	40 g/l

An electro-depositing solution of the above composition was used. Electro-deposition was effected onto a copper plate at an electric current density of 25 A/dm² for 50 seconds at a temperature of 30°C. An electro-deposit having a smooth surface was obtained in this way.

Electro-deposition was also effected onto annealed copper wire of a diameter of 1 mm using this electrodeposition solution at an electric current density of 25 A/dm² for 50 seconds at a temperature of 25°C. An electro-deposit having a plating thickness of 10 microns with variations in the plating thickness not exceeding 1 micron was obtained. This product had a good resistance to corrosion and scarcely any change in its colour was observed after it had been left standing in a room for 1 year. Its soldering property was also found perfect and no swelling at the solder wetting edges was observed.

Example 2

Instead of polyethyleneglycol-

nonylphenol ether used in Example 1, 10 g/l of either polyethyleneglycolisooctyl ether or polyethyleneglycol-lauryl ether or sodium *n*-octyl sulphate was added, and plating was effected under the same conditions as in Example 1. As a result, an electro-deposit which was as good as that of Example 1 was obtained.

Example 3

Divalent tin (as stannous oxide)	50 g/l	
Sulphamic acid	82 g/l	75
Polyethyleneglycolnonylphenyl ether (ethylene oxide average addition mol number 10)	10 g/l	
Orthophenolsulphonic acid	20 g/l	80

An electro-depositing solution of the above composition was used. Electroplating was effected onto annealed copper wire of a diameter of 1.2 mm at 20°C for 4 minutes with a current density of 5 A/dm². The electro-deposit obtained in this way had a smooth appearance. When the plating layer was heated and melted, no swelling was observed on the border between the molten part and the non-molten part. No sparking i.e. sparks of fire, was observed on melting when the tin-plated wire was put into a flame. In view of these properties, the tin-plating bath of the present invention is superior to the sulphuric acid bath and fluoborate baths that have previously been used.

Example 4

Divalent tin (as stannous sulphate)	114 g/l	100
Sulphamic acid	100 g/l	
Polyethyleneglycolnonylphenyl ether (ethylene oxide average addition mol number 8.5)	5 g/l	105
Cresolsulphonic acid	30 g/l	

An electro-depositing solution of the above composition was used. Electroplating was effected onto a copper plate with an electric current density of 20 A/dm² at a temperature of 25°C. The electro-deposit obtained in this way had a smooth appearance.

Example 5

Divalent tin (as stannous chloride)	40 g/l	115
Sodium sulphamate	16 g/l	
Sulphamic acid	20 g/l	
Polyethyleneglycolnonylphenyl ether (ethylene oxide average addition mol number 10)	10 g/l	120
Orthophenolsulphonic acid	20 g/l	

An electro-depositing solution of the above composition was used. Electroplating was effected onto annealed copper wire of a diameter of 1.2 mm at a current density of 5 A/dm² for 2 minutes at 20°C. The semi-lustrous electro-deposit obtained in this way had a plating thickness of 5 microns. It showed good results when tested for soldering properties.

The results of the tests for soldering properties of samples prepared by the method of this Example show that they possess the property of solder wetting and that they are entirely free from swelling at the edges of the solder wetting.

The electro-deposit obtained by plating at a current density of 10 A/dm² for 2 minutes had a plating thickness of 10 microns. Although it had no lustre, it had a smooth surface and gave good results when it was subjected to the tests for soldering properties.

The results of the tests for soldering properties of samples prepared by the method of this Example show that they are entirely free from swelling at the edges of the solder wetting.

Comparative Example

To illustrate the conventional method of plating electroplating was carried out with an electrolyte which had the following composition.

Divalent tin (as stannous fluoborate)	81 g/l
Fluoboric acid	100 g/l
Boric acid	25 g/l
Gelatin (dispersed after being swollen with water)	6 g/l
β -Naphthol (dispersed as an alcoholic solution)	1 g/l

The temperature of the solution was 25°C and the cathode current density 40 A/dm². Plating was effected onto soft copper wire of a diameter of 0.6 mm for 2 minutes, while stirring the solution. A plating layer of 10 microns was thus obtained. This product had a good appearance, but a large number of swellings occurred when it was heated for 30 minutes at 180°C.

Example 6

Divalent tin (as stannous oxide)	45 g/l
Sulphamic acid	82 g/l
Gelatin	5 g/l
Cresolsulphonic acid	20 g/l

An electro-depositing solution of the above composition was used. Plating was effected, with stirring, at 20°C at a cathode current density of 1 A/dm² to 50 A/dm² onto soft copper wire of a diameter of 1.2 mm.

Electro-deposits having a good smooth surface were thus obtained.

Of the electro-deposits obtained in this way, one of thickness of 10 microns prepared by deposition at 10 A/dm² for 2 minutes, was subjected to a soldering test. As a result of the test, it was found that it possessed perfect soldering properties. No swelling at all occurred at the edges of the solder wetting.

To prepare this electro-depositing solution, sulphamic acid and cresolsulphonic acid were first dissolved in the prescribed amount of water and stannous oxide was added to the solution and dissolved. Then, gelatin which had previously been swollen with water (about 100 ml of water is adequate for 5 g of gelatin) was added and mixed with stirring.

Example 7

Instead of the gelatin used in Example 6, 5 g/l of animal glue was used. Plating was effected under conditions within the same range of conditions as in Example 6, and an electro-deposit as good as that of Example 6 was obtained.

Example 8

Instead of orthophenolsulphonic acid used in Example 3, 20 g/l of parphenolsulphonic acid or 27 g/l of sodium parphenolsulphonate was added. Plating was effected under conditions within the same range of conditions as in Example 3, and an electro-deposit as good as that of Example 3 was obtained.

Example 9

Instead of orthocresolsulphonic acid used in Example 1, 45 g/l of sodium 1-naphthol-4-sulphonate or 45 g/l of sodium 1-naphthol-5-sulphonate was used. When plating was effected under conditions within the same range of conditions as in Example 1, an electro-deposit as good as that of Example 1 was obtained.

Example 10

Divalent tin (as stannous oxide)	90 g/l
Sulphamic acid	220 g/l
Orthocresolsulphonic acid	60 g/l

An electro-depositing solution of the above composition was used. Electro-deposition was effected at a temperature of 30°C and a cathode current density of 5 A/dm² for 3 minutes on a copper plate. An electro-deposit having a good smooth surface was thus obtained.

In all of these Examples, the material to be plated was subjected to the following pretreatment before plating.

5 It was first subjected to cathode electrolytic degreasing for 1 minute at an electric current density of 5 A/dm² at a solution temperature of from 60 to 80°C in an alkaline degreasing solution consisting of

caustic soda	15 g/l
sodium carbonate	40 g/l
sodium phosphate	30 g/l

10 and then rinsed with water. Then, it was immersed in a 20% aqueous solution of sulphuric acid for 30 seconds, and rinsed with water. After that, plating was made under the conditions mentioned in the Examples respectively.

15 In the Examples wherein a non-ionic surface active agent or anionic surface active agent was used, such an agent was used after previously adding thereto water in an amount of 3 to 20 times the volume of surface active agent and mixing by stirring.

20 All the tests of soldering properties carried out in the Examples were conducted in accordance with the MIL—Specification—202 C.

25 WHAT WE CLAIM IS:—

1. A tinplating solution which contains from 30 to 300 g/l of sulphamate ions, 15 to 300 g/l of divalent tin ions, and 5 to 100 g/l of an aromatic sulphonic acid having either an —OH radical or an —OH radical and a —CH₃ radical on the aromatic nucleus, or a salt thereof.

30 2. A tin-plating solution as claimed in claim 1 which includes therein from 1 to 30 g/l of a non-ionic or anionic surface active agent.

35 3. A tin-plating solution as claimed in claim 2 wherein the non-ionic surface active agent is polyethyleneglycol-nonylphenyl ether, polyethyleneglycol-isooctyl ether or polyethyleneglycol-lauryl ether.

40 4. A tin-plating solution as claimed in claim 2 wherein the anionic surface active agent is sodium *n*-octyl sulphate.

5. A tin-plating solution as claimed in claim 1 which includes therein 1 to 10 g/l of animal glue or gelatin.

6. A tin-plating solution as claimed in any one of the preceding claims wherein the sulphamate ions are derived from sulphamic acid, sodium sulphamate, potassium sulphamate or ammonium sulphamate.

7. A tin-plating solution as claimed in any one of the preceding claims wherein the aromatic sulphonic acid or the salt thereof is cresol sulphonic acid, phenol sulphonic acid, naphthol sulphonic acid or a sodium salt or potassium salt thereof.

8. A tin-plating solution as claimed in any one of the preceding claims wherein the divalent tin ions are provided stannous oxide, stannous sulphate or stannous chloride.

9. A tin-plating solution as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.

10. A method of plating a surface with a deposit of tin which method comprises electrodepositing a deposit of tin onto a substrate from an electroplating bath containing a tin-plating solution as claimed in any one of the preceding claims.

11. A method as claimed in claim 10 wherein the electro-deposition is effected at a temperature in the range of from 5 to 80°C and a current density in the range of from 1 A/dm² to 100 A/dm².

12. A method as claimed in claim 10 substantially as hereinbefore described with reference to any one of the Examples.

13. A tin-plated surface whenever prepared by a method as claimed in any one of claims 10 to 12.

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It was first subjected to cathode electrolytic degreasing for 1 minute at an electric current density of 5 A/dm² at a solution temperature of from 60 to 80°C in an alkaline degreasing solution consisting of

caustic soda	15 g/l
sodium carbonate	40 g/l
sodium phosphate	30 g/l

and then rinsed with water. Then, it was immersed in a 20% aqueous solution of sulphuric acid for 30 seconds, and rinsed with water. After that, plating was made under the conditions mentioned in the Examples respectively.

In the Examples wherein a non-ionic surface active agent or anionic surface active agent was used, such an agent was used after previously adding thereto water in an amount of 3 to 20 times the volume of surface active agent and mixing by stirring.

All the tests of soldering properties carried out in the Examples were conducted in accordance with the MIL—Specification—202 C.

WHAT WE CLAIM IS:—

1. A tinplating solution which contains from 30 to 300 g/l of sulphamate ions, 15 to 300 g/l of divalent tin ions, and 5 to 100 g/l of an aromatic sulphononic acid having either an —OH radical or an —OH radical and a —CH₃ radical on the aromatic nucleus, or a salt thereof.

2. A tin-plating solution as claimed in claim 1 which includes therein from 1 to 30 g/l of a non-ionic or anionic surface active agent.

3. A tin-plating solution as claimed in claim 2 wherein the non-ionic surface active agent is polyethyleneglycol-nonylphenyl ether, polyethyleneglycol-isooctyl ether or polyethyleneglycol-lauryl ether.

4. A tin-plating solution as claimed in claim 2 wherein the anionic surface active agent is sodium *n*-octyl sulphate.

5. A tin-plating solution as claimed in claim 1 which includes therein 1 to 10 g/l of animal glue or gelatin.

6. A tin-plating solution as claimed in any one of the preceding claims wherein the sulphamate ions are derived from sulphamic acid, sodium sulphamate, potassium sulphamate or ammonium sulphamate.

7. A tin-plating solution as claimed in any one of the preceding claims wherein the aromatic sulphononic acid or the salt thereof is cresol sulphononic acid, phenol sulphononic acid, naphthol sulphononic acid or a sodium salt or potassium salt thereof.

8. A tin-plating solution as claimed in any one of the preceding claims wherein the divalent tin ions are provided stannous oxide, stannous sulphate or stannous chloride.

9. A tin-plating solution as claimed in claim 1 substantially as hereinbefore described with reference to any one of the Examples.

10. A method of plating a surface with a deposit of tin which method comprises electrodepositing a deposit of tin onto a substrate from an electroplating bath containing a tin-plating solution as claimed in any one of the preceding claims.

11. A method as claimed in claim 10 wherein the electro-deposition is effected at a temperature in the range of from 5 to 80°C and a current density in the range of from 1 A/dm² to 100 A/dm².

12. A method as claimed in claim 10 substantially as hereinbefore described with reference to any one of the Examples.

13. A tin-plated surface whenever prepared by a method as claimed in any one of claims 10 to 12.

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